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Effect of dilute sulfuric acid hydrolysis of coconut dregs on chemical and thermal properties

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Abstract

Coconut dregs is a residue of coconut milk production, have no others usage except as animal food. It contains main components of lignocellulosic materials and high carbohydrate content. However, there are lack of study and understanding regarding properties of coconut dregs as useful products. In addition, the physical and chemical barriers due to the complex bonds of cellulosic compound hinder the hydrolysis hemicelluloses and cellulose into fermentable sugars. Thus, the main purpose of this study was to investigate the hydrolysis of coconut dregs for the production of glucose at various times. Coconut dregs were subjected to dilute sulfuric acid (1%) hydrolysis at 130°C and varying hydrolysis time (30, 60 and 90 min). The prehydrolyzate from this process was characterized by Biochemistry analyzer for glucose concentration analysis. Higher glucose concentration (0.38 g/l) was reached at a residence time of 60 min. Chemical and thermal properties of the solid residue were also carried out. The results demonstrated a reduction in chemical and thermal of solid hydrolyzed fraction compared to raw state. Meanwhile, FTIR spectra revealed no significant changes in cellulosic compound when coconut dregs were hydrolyzed at different time. TGA and DTG analysis showed almost similar range of cellulosic compound degradation temperature after hydrolysis.

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1. Introduction

Lignocelluloses biomass are cheap, largely unused, renewable and the most abundantly available sources[1-2]. These resources are an alternative resource in replacing the chemical feedstock that affect the environmental, long-term and national security concerns[3]. A number of lignocelluloses materials like biomass waste, agricultural wastes, forest residues, waste paper and municipal solid waste are mainly made up of carbohydrate [2, 4-5]. Other than carbohydrate, these feedstocks contain of extractives and ashes[2].

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The most studied of these feedstock for the purpose of replacement as energy source was switchgrass and poplars[6]. However, another viable lignocelluloses feedstock is biomass waste. The biomass waste under consideration in this study is coconut dregs. Coconut dregs were used mainly as animal feed, abundant and can be obtained at low cost or no cost. This feedstock was leftover from coconut milk production and contains high value of carbohydrate[7].

Lignin, hemicelluloses and cellulose are the main components in the carbohydrates polymer of lignocelluloses feedstock[2]. Predominant component in this material is cellulose followed by smaller amount of hemicelluloses and lignin [8]. Cellulose comprises D-glucose subunits linked to each other by β-(1,4)-glycosidic bonds. It is packed into microfibrils formed from the long chain cellulose polymers that linked together by hydrogen and van der Waals. Hemicelluloses and lignin form a hydrogen bonds with microfibril of cellulose[9].

Main difference between hemicelluloses and cellulose is hemicelluloses contain branches with short lateral chains consisting of monosaccharides. The monomeric sugars in the hemicelluloses include pentoses, hexoses and uronic acids. Hemicelluloses that consists of short bonds linked by β-(1,4)-glycosidic bonds and occasionally β-(1,3)-glycosodoc bonds is more easily hydrolysable compared to the celluloses. Lignin has a complex structural, act as a resistance against microbial attack, imparting structural support and mostly present in the primary cell wall[9]. Monomer sugar like glucose can be depolymerized through either the action of acid hydrolysis or enzyme[2]. The common method to break down these sugars from cellulosic materials is enzymatic hydrolysis. However, enzymatic hydrolysis required high economics considerations wherein crucial additional step involve that is pretreatment[6]. Pretreatment is used to break down the hemicelluloses into its monomeric sugars, reduce crystallinity of the cellulose and increase the porosity of the feedstocks[10].

Dilute acid hydrolysis has received considerable researched attention as it is inexpensive and effective[9]. Almost 100% of hemicelluloses are completely removed when sulfuric acid is mixing up with cellulosic biomass. The common acid used is sulfuric acid in which it enhances the digestibility of the cellulose operate in high temperature[9]. Hydrolysis of sulfuric acid in the lignocelluloses materials with concentration of 0.5-1.0%, operate at moderate temperature can dissolve almost of hemicelluloses into sugars and dissolved lignin partially[11]. It can be performed at moderate temperature (<160°C) for longer hydrolysis time (30-90 min)[9, 12].

However, the effects of hydrolysis time of coconut dregs by dilute sulfuric acid on the chemical and thermal properties have not been investigated at present. Therefore, the main aim of this study was to investigate the effects of hydrolysis time on the glucose concentration of coconut dregs produced. A second aim of this study was to determine chemical changes and thermal decomposition on the cellulosic compound of coconut dregs. For these proposes, Biochemistry analyzer was employed in order to determine the glucose produced after hydrolysis. Moreover, thermal properties of raw state and the hydrolyzed of coconut dregs were investigated using Thermogravimetric infrared (TGA). Other than that, the possible structural changes in the cellulosic compound before and after hydrolysis was analyzed by Fourier transform infrared (FTIR) spectra.

2. Experimental

2.1. Materials and Chemicals

Coconut dregs were obtained from wet market, Shah Alam, Malaysia. The collected substrate was soaked in distilled water to remove the impurities at ambient temperature for 24h. The soaked coconut dregs was then dried in an oven for 16h at 105°C and stored in sealed plastics bags for further process.

2.2. Sulfuric Acid Hydrolysis

Coconut dregs were sieved before hydrolysis and the particle size of coconut dregs less than 2mm was used. Dilute sulfuric acid was carried out using 1 L shake flask in an autoclave (Hirayama). 4g of dry coconut on a dry basis was mixed with 200 mL of 1% sulfuric acid at 130°C and various hydrolysis times. Different times for dilute sulfuric acid hydrolysis, namely as 30, 60 and 90 min were applied first to determine higher concentration of glucose. At the end of the hydrolysis, liquid fraction from hydrolyzate was filtered using Filtres Fioroni (601) to determine glucose concentration. The residual part was dried overnight at 60°C for chemical and thermal analysis.

2.3. Analysis

Moisture content of the coconut dregs was determined by drying the sample at 105°C in an oven until total weight change less than 0.2% and recorded as final weight. Glucose content from the hydrolyzate was measured using Biochemistry Analyzer (YSI2700) equipped with a standard of dextrose. Fourier transform infrared (FTIR) spectra were used to evaluate the cellulosic compound resulting from dilute sulfuric acid hydrolysis. This analysis was performed using a PerkinElmer FTIR Model Spectrum One in the range of 600 to 4000 cm^{-1}. Thermal properties were analyzed by Thermogravimetric analysis (TGA)). This thermal stability was investigated using Mettler Toledo thermogravimetric analyzer. The decomposition analysis was performed under nitrogen and air atmosphere in an constant flow of 120 cm^3/min, with heating range of 10°C/min, sample mass of 20 mg and temperature programs from room temperature to 900°C.

3. Results and discussion

3.1. Content of glucose

Fig. 1 is represents different time of coconut dregs was hydrolyzed using 1.0% sulfuric acid. Ratio of solid to liquid was 1:50(w/v) was carried out under different hydrolysis time (30, 60 and 90 min) at 130°C. The glucose concentration slightly increased with hydrolyzed time for 30 min and 60 min from 0.31 g/l to 0.38 g/l. The results obtained were in an agreement with those studied on the glucose produced from lignocellulosic biomass with different nature of feedstock and operation parameters[5, 8]. The increment in glucose concentration resulted in increase of solubilization and degradation of hemicelluloses occurred after the dilute sulfuric acid hydrolysis[10].

Glucose is the second intermediate product in the conversion of biomass in the sequence of: cellulose to oligosaccharides and finally break down into hexose (glucose). Further reaction of consecutive reaction will lead to decomposition of 5-hydroxymethyl-furfural (5-HMF)[13]. Thus the hydrolysis time was varied to optimize the reaction condition to avoid the production of this furfural as hydrolysis time affect the formation of furfural. The results represented in Fig 1. indicated that the best hydrolysis time to get higher glucose was applying 60 min for dilute sulfuric acid hydrolysis. On the other hand, the hydrolysis efficiency by prolonged autoclaving time to 90 min was decreased, indicated that this residence time was not suitable for solubilization of monomeric sugars in coconut dregs. Moreover, this can be explained by the production of number of furfural formation resulted from higher temperature of acid hydrolysis[2]. It has previously been demonstrated that acid hydrolysis converts these components into accumulation of furfural in the prehydrolysate under undesired reaction conditions[3].

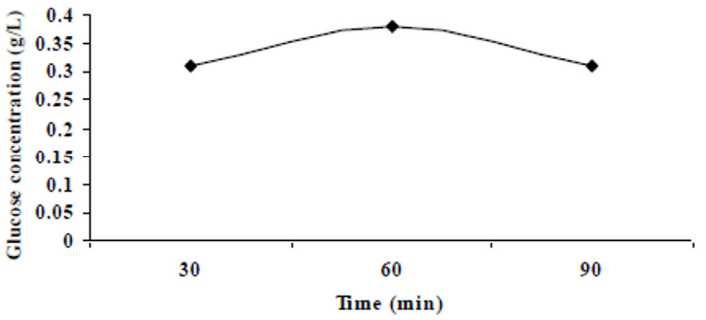

Fig. 1. Effect of dilute sulfuric acid hydrolysis time on glucose

3.2. FTIR spectra

The chemical structure of the raw state and hydrolyzed of coconut dregs after various hydrolysis times was investigated using FTIR spectra. The broad peaks around 3350-3366 cm^{-1} were assigned to the hydroxyl group stretching vibrations of cellulose. Absorbed water, aliphatic primary and secondary alcohols found in cellulose, hemicelluloses, lignin and extractives were included in this region. Fig. 2(b) shows the intensity at the O-H band was lower than other samples due to the scission of the intra- and intermolecular hydrogen bonds. As hydrolysis time increase, the intensity at the peaks of 2853 and 2922 cm^{-1} were decreased. This range of bands indicated to C-H stretching within the cellulose. The methylene of cellulose was lower in intensity after hydrolysis and almost disappeared when hydrolyze at 30 min hydrolysis. One explanation for this could be the crystalline cellulose in the coconut dregs was not disrupted by acid hydrolysis[1].

The peaks ranging from 1000 to 1200 cm^{-1} were indicated to the structural of hemicelluloses. Absorbance at 1010, 1030 and 1031 cm^{-1} were identified to primary OH associated with hemicelluloses and was not easily disrupt by acid hydrolysis[1, 14-15]. The peaks at 1742 and 1743 cm^{-1} showed the presence of C=O stretching originated from carbonyl and acetyl ester bonds of hemicelluloses. The peaks disappeared after hydrolysis indicated that most of the hemicelluloses were removed during hydrolysis. This is expected as the dilute sulfuric acid hydrolysis is known to affect the removal of hemicelluloses[3]. These results were in agreement with a previous study which reported that hemicelluloses was easily dissolved by acid hydrolysis[1, 3]. However, the occurrence of the peaks at 1153 and 1152 cm^{-1} correspond to the structural features of hemicelluloses and represented ester group of hemicelluloses[16]. The presence of these peaks implied that a C-O-C glycosidic vibration at these peaks was not easily cleaved by acid-catalyzed reaction. β-glycosidic linkages between the sugar unit in hemicelluloses were indicated in all sample at the small band in the anomeric region ranges between 950-700 cm^{-1}[11].

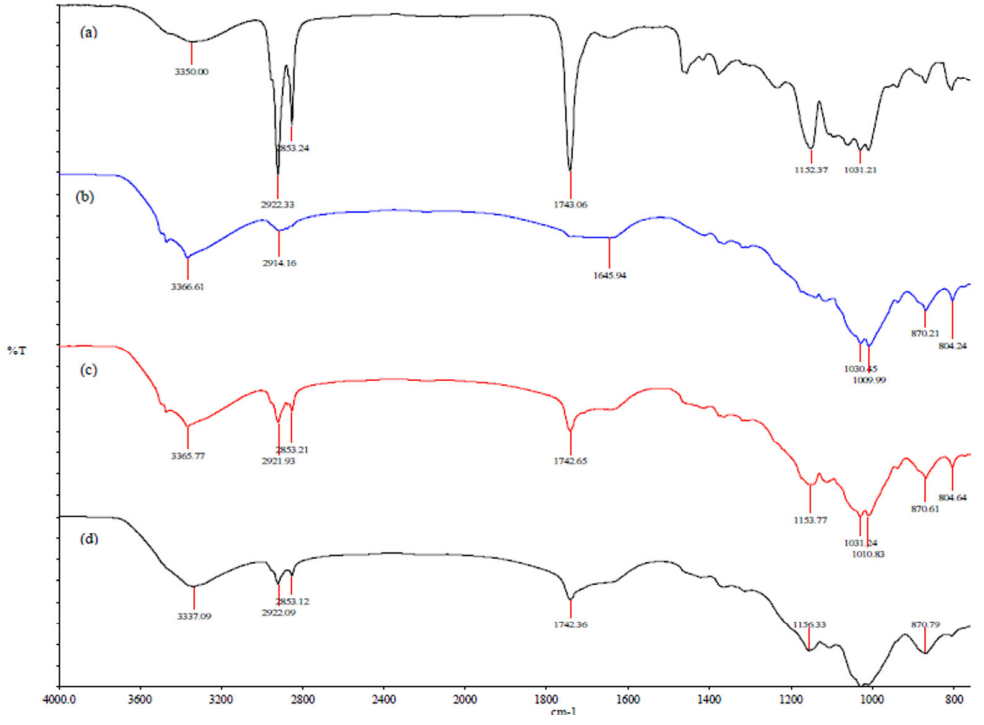

Fig. 2. FTIR spectra of (a) raw state, hydrolysis of coconut dregs for (b) 30 min, (c) 60 min and (d) 90 min

Only for retention time of 60 min showed a fall in intensity or almost disappeared of these peaks and a peak of 1645 cm^{-1}. This peak show in Fig. 2.(b) is assigned to the alkyl group of lignin side chains and conjugate to aromatic skeleton of sulphonic acid[1]. The intensity of this peak disappeared in other samples implied that hydrolysis of acid may cause degradation of β-O-4 linkages or another bond rearrangement that results in increased carbonyl groups within the lignin component[4]. In addition the appearance of lignin might be due to the removal of hemicelluloses and lignin was released and re-deposited on the surface[2]. When comparing the results, it appears that the intensity of the peaks were decreased with the increased hydrolysis time due to the lignin, hemicelluloses and cellulose dissolution during acid hydrolyzed reaction[1].

3.3. Thermal analysis

The weight loss and derivative (DTG) curves of native and after hydrolysis of coconut dregs are shown in Fig. 3. Thermal decomposition of this lignocellulosic material is strongly depends on the hemicelluloses, cellulose and lignin[17]. The dilute acid hydrolysis improved the thermal stability for coconut dregs when compared to its raw state. Moisture loss started its decomposition from room temperature to 105°C. However, great differences were found among the degradation of these three components in the raw state and the samples after hydrolysis. The weight value observed was higher after coconut dregs were hydrolyzed with sulfuric acid. From thermogravimetric (TG) analysis, the total weight loss in the sample after hydrolysis falls in the range of 7-12% which was higher than the native of coconut dregs. This was probably due to the reduced amounts of cellulosic compound to form hydrogen bonds with water. However, the initial weight loss in the sample after hydrolysis was followed by the vaporization of bound water in the samples after hydrolysis[18]. This process corresponds to the presence of water in samples as occluded surface adsorbed moisture or chemically hydrates[19]. In addition the presence of the bound moisture in these samples was due to the effect of sulfuric acid used in the hydrolysis. This is similar to the TG analysis of sulfuric acid exhibited a peak at this range of temperature from the previous study[20].

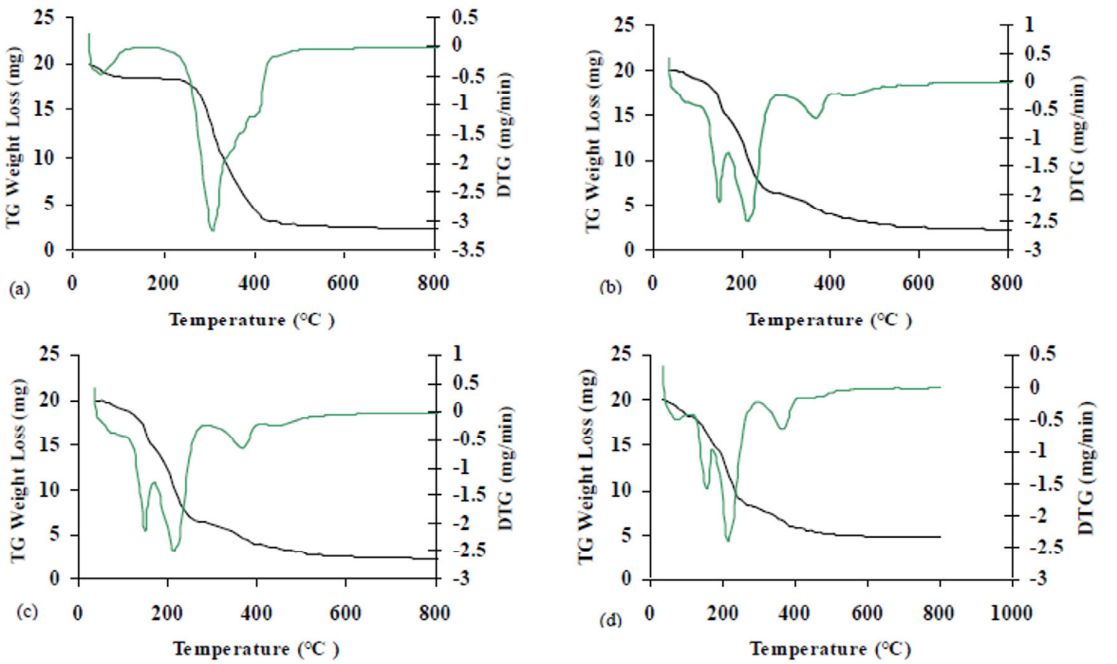

Fig. 3. TGA(—) and DTG(—) at four heating rates for (a) raw state of coconut dregs, hydrolysis of coconut dregs for (b) 30 min, (c) 60 min and (d) 90 min

Hemicelluloses is the less stable amongst the lignocellulosic components and it starts degrade at lower temperature between 150 - 315°C[21]. Hemicelluloses decomposition for raw state was focused at temperature of 220-340°C with the weight loss of 81%. Nevertheless, the effect of sulfuric acid hydrolysis contributes to the lower degradation temperature of hemicelluloses at 170-280°C. The decomposition temperature was decreased probably due to the degradation of amorphous structure of hemicelluloses and sulfuric acid was easily hydrolyzed this components[22]. As hydrolysis time increased, the peak of hemicelluloses more narrow due to the rapid decomposition of the hemicelluloses. This happened might be due to the hemicelluloses is rich in branches of monosaccharides wherein easily removed from the main stem and can be easily degraded at high temperatures[23].This decomposition of hemicelluloses was in agreement with FTIR analysis as discussed above.

In contrast with hemicelluloses, cellulose is crystalline, strong, thermal stability is high and has a long polymer of glucose without branches[22-23]. For all samples, cellulose decomposed in the range of 315-400°C. After hydrolysis, the decomposition peaks for cellulose obviously exhibited. This indicated that sulfuric acid hydrolysis successfully fractionated into the degradation of hemicelluloses, cellulose and lignin[15]. When the temperature was higher than 200°C, almost all lignin was slowly decomposed for the whole temperature up to 900°C[24]. Among these three components, lignin was difficult to decompose due to the content of three kinds of benzene-propane and is heavily cross linked. Upon discussion of the above observations, these three components was degraded from the most difficult to the easiest in the thermal degradation was hemicelluloses > cellulose > lignin[22].

4. Conclusion

The results indicated that higher glucose concentration, 0.38g/l can be obtained from the hydrolysis with time of 60 min. Approximately 1.9% of glucose yield was recovered from hydrolysis of coconut dregs with 1% sulfuric acid solution. This hydrolysis depends on variables of hydrolysis time and the results directly affect the thermal and chemical properties. Great differences of the hydrolyzed and raw state of coconut dregs were shown from the FTIR and TGA analysis. From TGA analysis, lignin was degraded at whole temperature from room temperature to 900°C. The easiest component to be decomposed was hemicelluloses, which was happened at 150-315°C and degradation of cellulose was happened at 315-400°C. Nevertheless, coconut dregs after hydrolysis showed two peaks at temperature below 200°C indicated that the moisture loss and rebound moisture. The appearance of these peaks after hydrolysis might be due to the attachment of water to the surface of sample due to the presence of sulfuric acid. The results obtained through FTIR showed that degradation of lignin, hemicelluloses and cellulose occurred between raw state and hydrolyzed coconut dregs. Thus, this waste that is abundantly available in Malaysia has the potential to serve as a low cost glucose feedstock.

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